Enhancement in Activity and Reusability of Dry Amberlyst-15 Catalyst by Thermal Treatment for Production of Biodiesel from Karanja Oil

Arun Kumar Gupta[*,iD] and Goutam Deo[iD]

Department of Chemical Engineering, University Institute of Engineering and Technology, C.S.J.M. University, Kanpur-208024, India

*Corresponding author: E-mail: arunkgupta@csjmu.ac.in

The effect of preheating Amberlyst-15 catalyst used for the biodiesel production reaction of Karanja oil was studied. The preheated Amberlyst-15 samples were characterized for their surface area and pore volume and by SEM, TGA and FTIR spectroscopy. A preheat temperature of 473 K was found to optimum. At this temperature, the surface area had increased and the sulfonic acid groups of Amberlyst-15 were retained. At 473 K preheated Amberlyst-15 gradually deactivated with reuse from a biodiesel yield of 85% to 27% in four runs at a reaction temperature of 393 K and methanol to oil ratio of 60:1. For the power-law model, the reaction order was 0.65, the rate constant at 373 K was 0.027 h^{-1} and activation energy was 86.98 kJ/mol.

Keywords: Biodiesel, Karanja oil, Amberlyst-15, Reusability, Kinetic parameter.

INTRODUCTION

Biodiesel is used as a alternative fuel or as blend in fuel applications. Biodiesel productions from the non-edible oil are encouraged due to various global and economical reasons [1-3]. This is among the non-edible oils available in India from the Karanja tree (Karanja oil), which is widely available in the Indian subcontinent and has shown great potential as a source for biodiesel production [4-8]. Acid catalysts are ideally suited for converting non-edible oils since they contain a high percentage of free fatty acids (FFAs) [2,9]. Alternatively, a two-step process can be used for biodiesel production from non-edible oils. In this two-step process, the first step is used to convert the FFAs by using a acid catalyst and the second-step is then used to convert the pretreated non-edible oil by a base catalyst [4,5,7,10]. However, two-step processes were shown not economical for the biodiesel production [11,12]. The one-step process can be further developed using solid acid catalysts [13]. Solid-phase or heterogeneous acid catalysts have certain advantages over liquid-phase or homogeneous acid catalyst [14,15]. These advantages include ease of separation, purity of product and decrease in the number of processing steps [16]. However, a suitable heterogeneous acid catalyst should be tested for deactivation and effects of transport of material to and from the active

sites [14]. Several heterogeneous acid catalysts have been reported [13,14,17]. Amberlyst-15 is a sulfonic acid cation exchange resin containing styrene divinylbenzene copolymer and has been often used for biodiesel production [18-20].

Homogeneous and heterogeneous base catalysts have been used extensively for the conversion of Karanja oil to biodiesel. However, the application of heterogeneous acid catalyst to the conversion of Karanja oil to biodiesel is restricted to a part of one study [21]. In this study heterogenous catalysts, such as Hβ-zeolite, montmorillonite K-10 and ZnO, were used and the results from homogeneous base and heterogeneous catalysts for the conversion of Karanja oil were compared. It was reported that the heterogeneous catalyzed process was much slower and required higher temperatures. A biodiesel yield of 83% was reported over ZnO and 47% and 59% over montmorillonite K-10 and Hβ-zeolite after 24 h of reaction at 120 ºC. This was compared to the 90% to 95% biodiesel yield achieved at 60 ºC using a homogeneous base catalyst (KOH) along with a co-solvent.

In present study, Amberlyst-15 was used as a heterogeneous acid catalyst for the conversion of Karanja oil to biodiesel. Specifically, attempts were made to increase the activity by pretreating Amberlyst-15 at higher temperatures. The effect of preheating at higher temperatures was analyzed by scanning electron microscopy (SEM), surface area and pore volume analysis and

FTIR characterization. The effect of reusing and regenerating the preheated Amberlyst-15 catalyst was also examined. Kinetic studies for the conversion of Karanja oil to biodiesel were accomplished by estimating the reaction parameters, such as rate constant, order of the reaction and activation energy.

EXPERIMENTAL

The Karanja oil was purchased from the local market of Kanpur city, India. Methanol (99% purity, Merck) was used as alcohol source and dry Amberlyst-15 (moisture up to 5%, Sigma-Aldrich) was used as catalyst. All the chemicals were used as-received for the biodiesel production reaction.

Reactor setup: A stainless-steel batch reactor of 2 L capacity (length 30 cm, diameter 15 cm) with impellor (dia. 6 cm) was used for biodiesel production in this study. The reactor temperature was sensed and controlled by a PT-100 temperature sensor attached to a PID controller (Selec, Model PID 500). The reactor was electrically heated. A cooling water circulation system was also provided for proper temperature control. Samples of the reaction mixture could be withdrawn from the valve situated at the bottom of reactor. Previous studies [22,23] also used the same batch reactor for biodiesel production .

Catalyst characterization: Scanning electron microscopy (SEM) studies were done using a TESCAN (MIRA3) instrument under high vacuum mode using an SE detector and 5 kV beam voltage. Fourier transform infrared (FTIR) spectroscopy (Perkin-Elmer spectrum) was used to detect the presence of functional groups in the catalyst. The FTIR spectrum was obtained under ambient conditions and recorded from 2000 to 400 cm^{-1} using 32 scan. Amberlyst-15 catalyst was ground with a mortar and pestle, mixed with KBr, pelletized and loaded on to FTIR holder for analysis. The surface area, pore volume and pore size distribution of the catalyst was measured using an Autosorb-1C instrument (Model: AS1-C, Quantachrome, USA).The Brunauer, Emmett and Teller (BET) surface area was measured by multiple point method. Prior to adsorption the sample was out gassed at 393 K. Nitrogen gas was used for adsorption-desorption at 77 K.

The as-received Amberlyst-15 was preheated at different temperatures in a muffle furnace. The as-received or preheated Amberlyst-15 was mixed with the known amount of Karanja oil and methanol in the batch reactor. The total volume of the reactant mixture was kept constant. The lid of the batch reactor was sealed to avoid vibration and leakage at high agitation speeds. After sealing the reactor the mixture of reactants and catalyst was heated to the desired reaction temperature. The reaction mixture was agitated at 750 rpm during the heating process. The heating rate was such that the reaction mixture took about 1 h to reach set point. The reaction time was measured after reaching the set point and the reaction was continued for 8 h [24]. Intermediates samples were withdrawn after known time intervals and kept in an ice-bath to quench the reaction. After 8 h of reaction, the heating was stopped and the reactor vessel was allowed to cool to room temperature. All the collected samples for analysis were washed several times with hot double distilled water (about 70 ℃). The separated samples, free from

methanol and water, were analyzed with ^{1}H NMR spectroscopy. From the areas of methyl group (α-CH$_2$), ester (-CH$_3$), glyceridic peaks the biodiesel yields was obtained using established procedures [25]. The effects of different parameters *viz.* preheated temperature of catalyst, amount of catalyst, reusability of the catalyst, regeneration of the catalyst and reaction temperature were studied.

Estimation of kinetic parameters: Before estimating the kinetic parameters the observed reaction rates were tested for external and severe internal mass transfer effects using Meirs and Weisz-Prater criteria [26]. In the absence of mass transfer effects the kinetic parameters were estimated. The kinetic study for the biodiesel production reaction was done using Polymath 5.1 and the kinetic parameters were estimated by non-linear regression analysis. A power-law model for the reaction was considered for the estimation of kinetic paratmeters. To estimate the kinetic parameters of the power-law model the biodiesel formation reaction was carried out with preheated Amberlyst-15 at 353, 373 and 393 K and a methanol to oil ratio of 60:1. The concentration of α-CH$_2$, glyceridic and methyl ester protons were tracked as the reaction progressed and the biodiesel yield and conversion of glyceridic groups were calculated. From the biodiesel yield and the glyceridic conversion the concentration of triglyceride + diglyceride + monogyceride remaining in the reaction mixture was determined. During this analysis, it was assumed that the direct conversion of glycerides to biodiesel occurred. It was also assumed that the effect of pressure on the reaction was negligible though the pressure of the sealed reactor vessel were estimated to be about 6 bar. The rate of consumption of glycerides was related to the concentration of glycerides by the following equation:

$$-r_G = kC_G^n \qquad (1)$$

where, k is the rate constant and n is the order of the reaction. In the above power-law model, the concentration of methanol was assumed to be in excess and was relatively constant during the course of the reaction. Consequently, the concentration of methanol could be included into k. An Arrhenius type of relationship was considered for k *i.e.*

$$k = k_o \exp\left(-\frac{E}{RT}\right) \qquad (2)$$

where, k_o was the pre-exponential factor, E was the activation energy, R was the universal gas constant and T was the reaction temperature.

The values of k and n at each temperature were estimated from the experimental data by the integral analysis. Non-linear regression of the power-law model was then applied for a better estimate of the kinetic parameters. Previous studies reparameterized the rate constants to decrease the correlation between k and E [27]. Thus, before non-linear regression the rate constant was re-parameterized as:

$$k = k_m \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \qquad (3)$$

where, k_m was the rate constant at a mean reaction temperature of T_m. The value of T_m in the present study was 373 K. Thus,

the modified power law model used for estimating the kinetic parameters by non-linear regression was

$$-r_G = k_m\, C_G^n \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \qquad (4)$$

The initial values of k_m, n and E that were required for non-linear regression were obtained from the estimates at each temperature given above.

RESULTS AND DISCUSSION

Physical characterization of preheated Amberlyst-15: Thermogravimetric analysis revealed the three distinct regions of weight loss (Fig. 1). The first region (peak at 360 K) was attributed with the removal of adsorbed moisture [28], whereas the second and third regions were attributed with the removal of sulfonic acid groups of Amberlyst-15 catalyst. Based on this derivative thermogam, two different preheated temperatures *viz.* 473K and 573 K were considered in the present investigation.

To study the thermal stability, Amberlyst-15 was heated at 473 and 573 K and then characterized by obtaining the SEM micro-graphs, BET surface area and pore size distribution analysis. The SEM micrographs (Fig. 2a-f) revealed that the particle size and pore size decreased with increase in temperature. Amberlyst-15 diameter decreased from about 800 µm
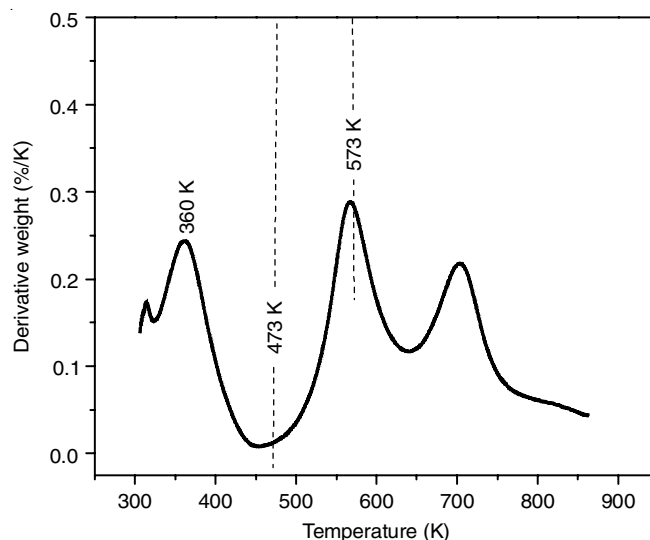

Fig. 1. Derivative plot of TGA data showing the weight loss at different temperatures. The preheat temperatures used are shown as dotted lines

for the as-received catalyst at 298 K, to about 500 µm for the catalyst preheated at 473 K and to about 250 µm for the catalyst preheated at 573 K. The pore size also decreased with increase in temperature and at 573 K and the catalyst appeared to be non-porous as shown in Fig. 2f.
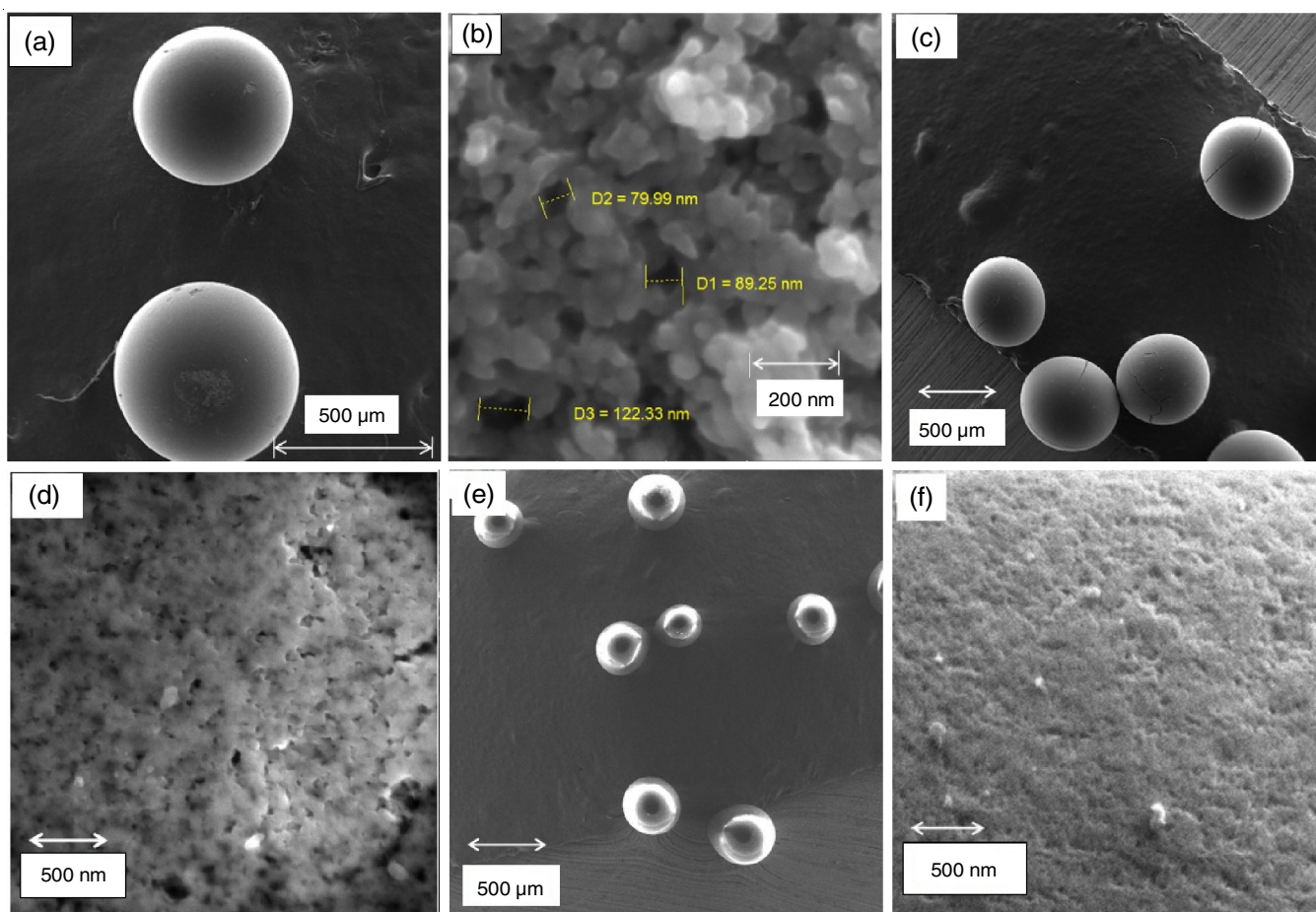

Fig. 2. SEM micrographs of the size of Amberlyst-15 as a function of calcinations temperature

The surface area and the pore volumes of Ambelyst-15 calcined at different temperatures were determined and the values are given in Table-1. The surface area of Amberlyst-15 increased from 70 to 300 m²/g when the temperature was increased from 298 to 573 K. However, the total pore volume initially increased and then decreased when temperature was increased from 298 to 573 K. A total pore volume of 0.94 cc/g was observed at 473 K. Analysis of the different pore volumes revealed that mesopores (pore between 2 nm and 50 nm) were predominantly present in the as-received Amberlyst-15 sample. Upon calcination the fraction of the total pore volume as meso-pores decreased and the fraction as micro and macro pores increased. At 573 K, the Amberlyst-15 sample had 25% of the total pore volume as micropores and about 2% as macropores.

TABLE-1
EFFECT OF PREHEAT ON THE
AS-RECEIVED AMBERLYST15 CATALYST

Preheat temp. (K)	BET area (m²/g)	Pore volume (cc/g)			
		Total	Micro-pore	Meso-pore	Macro-pore
As-received	70	0.50	0	0.49	0.01
473	113	0.94	0	0.91	0.03
573	300	0.57	0.14	0.42	0.01

FTIR studies: The FTIR spectra (Fig. 3) revealed the presence of vibrations due to water, hydroxyl and sulfonic groups. With increase in temperature all the peaks decreased in intensity and at 573 K, the complete removal of sulphonic group was observed. However, the decrease in intensity of various bands for the as-received Amberlyst-15 and the Amberlyst-15 at 473 K may be due to the inherent charact-eristic of the sample and not due to the decrease in amounts of various vibrating groups.
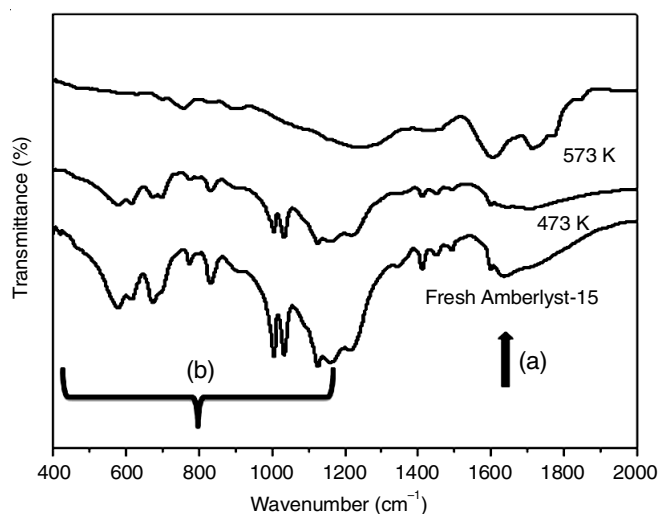

Fig. 3.   Comparison of the FTIR spectra of as-received and preheated Amberlyst-15 catalyst showing (a) moisture and hydroxyl bands at 1638 cm⁻¹ and (b) sulphonic groups bands at 410, 580, 676, 776, 834, 1035 and 1127 cm⁻¹

Biodiesel yield with preheated Amberlyst-15: The production of biodiesel from Karanja oil was studied by using the Amberlyst-15 catalyst at 473 and 573 K and the results were compared in Fig. 4 with those obtained by using the as-received
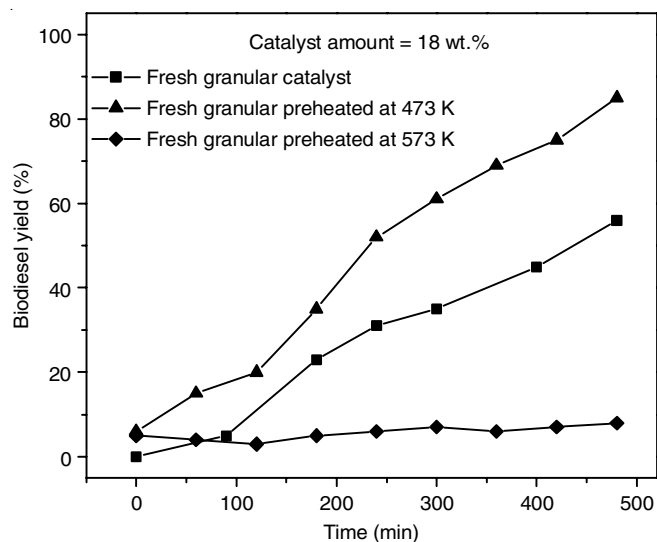

Fig. 4.   Biodiesel yield at different reaction times showing the effect of using preheated Amberlyst-15 catalysts. Reaction condition: T = 393 K; methanol:oil = 60:1; rpm = 750; reactant volume = 341 mL; catalyst amount = 18 wt.%

Amberlyst-15 catalyst. The conversion of the glyceridic proton was also analyzed. The biodiesel yields determined by analyzing the α-CH$_2$ and methyl ester protons and the glyceridic conversions determined by analyzing the glyceridic and methyl ester protons, differed by less than 2% indicating the absence of side products.

Fig. 4 revealed that the biodiesel yield increased monotonically with time for the as-received and the 473 K preheated Amberlyst-15 catalyst. The biodiesel yield achieved was 56% after 8 h of reaction when the as-received Amberlyst-15 catalyst was used as the catalyst. In comparison, the biodiesel yield achieved was 85% after 8 h when the Amberlyst-15 preheated at 473 K was used as catalyst. At 573 K preheated Amberlyst-15 cata-lyst the biodiesel yield was low and relatively constant at 8%.

The characterization results of Amberlyst-15 catalyst at 473 K revealed that a higher surface area was available for reaction. Furthermore, the sulfonic acid groups appeared to be retained at 473 K. The presence of sulphonic acid groups and increase in surface area indicated that more acid sites were available for the catalytic conversion of Karanja oil to biodiesel. Consequently, the biodiesel yield was high. In contrast, the 573 K preheated Amberlyst-15 catalyst low yields of biodiesel was obtained. Despite an increase in surface area, this sample lost sulfonic acid groups. The absence of sulfonic acid groups despite the increase in surface area reflected that sulfonic acid groups were the catalytic active sites and their absence resulted in an inactive catalyst. Thus, the high catalytic activity of Amberlyst-15 catalyst heated at 473 K appeared to be related to a higher surface area and the presence of sulfonic acid groups.

Stability of Amberlyst-15 catalyst: The SEM micro-graphs of 473 K preheated Amberlyst-15 catalyst was compared with the spent Amberlyst-15 catalyst. Fig. 5 revealed that the insignificant amounts of disintegration of the Amberlyst-15 catalyst had occurred. Furthermore, the catalyst size before and after reaction were similar, indicating that the physical structure of the preheated Amberlyst-15 catalysts was retained
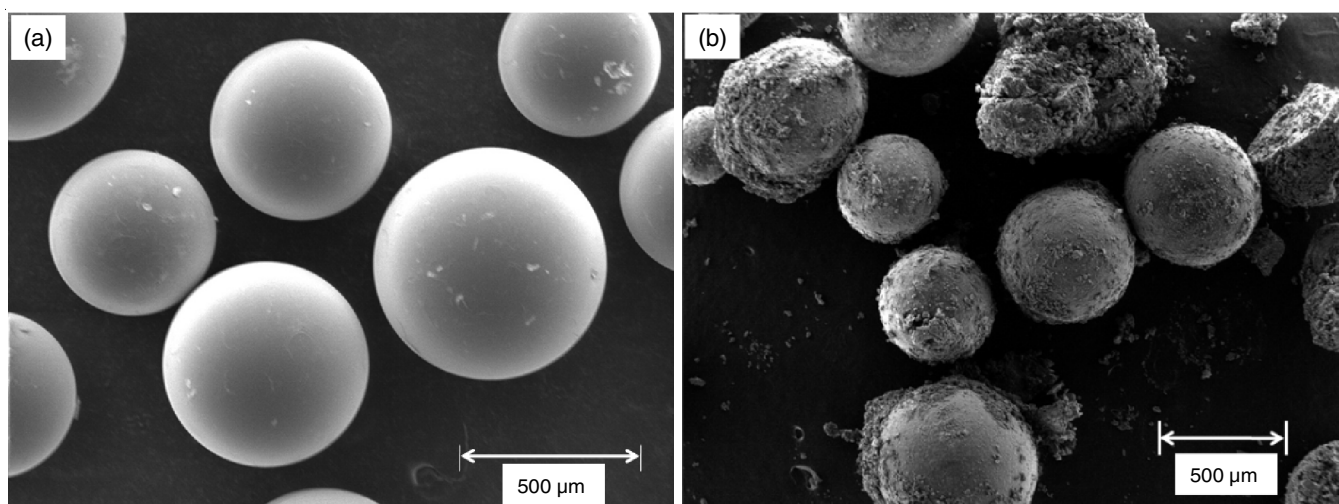
Fig. 5. SEM analysis of the (a) fresh and (b) spent preheated Amberlyst-15

during the reaction. Analysis of pore sizes and surface area of the spent catalyst was difficult to achieve due to the present of reactants and products on the catalyst surfaces and a complete analysis of the spent catalysts was not possible. It was shown that as-received Amberlyst-15 catalyst disintegrated in methanol to oil ratios greater than 6:1. Thus, preheating at 473 K increased the catalytic activity as well as the stability of catalyst.

Effect of reuse and regeneration of pre-heated Amberlyst-15: The activity of the preheated Amberlyst-15 catalyst was also tested for deactivation. During the reusability experiments, the same catalyst was separated from the reaction mixture after 8 h of reaction and reused with a fresh stock of reactants.

Table-2 revealed that with reuse there was a loss in the catalyst activity. The biodiesel yield decreased from 87% to about 27% when the 473 K preheated Amberlyst-15 catalyst was reused 4 times. After reusing 4 times, the catalyst was removed and heated at 473 K for 4 h. The heated catalyst was used again with a fresh stock of reactants. Interestingly, the regenerated catalyst showed a higher biodiesel yield of about 95% compared to 87% biodiesel yield achieved during the fresh preheated Amberlyst-15 catalyst. The reversible deactivation appears to be due to adsorbed species that are removed when the spent Amberlyst-15 catalyst was heated again at 473 K. Analysis of the spent catalyst by TGA and FTIR were inconclusive due to the presence of reactants and products as shown in the SEM micrograph of the spent catalyst as shown in Fig. 5.

TABLE-2
CHANGE IN BIODIESEL YIELD
WITH REUSE AND REGENERATION

Type of catalyst	Biodiesel yield (%)
Fresh 473 K preheated Amberlyst 15	87
Used catalyst of the 1st run	39
Used catalyst of the 2nd run	40
Used catalyst of the 3rd run	27
Used catalyst of the 4th run heated at 473 K	95

Reaction conditions: Catalyst amount = 18 wt% of oil; temperature = 393 K; rpm = 750; time = 8 h; methanol:oil = 60:1, reactant volume = 341 mL

Effect of catalyst amount: To ensure that amount of catalyst was sufficient for achieving the highest biodiesel different amount of 473 K preheated Amberlyst-15 catalyst was used while keeping the other reaction conditions constant. Table-3 revealed that the biodiesel yield increased with increase in amount of catalyst till 4.5 wt%. Beyond that, the biodiesel yield was relatively constant. The almost linear increase in biodiesel yield with weight of catalyst was indicative of the relatively constant turnover number (TON). Assuming that the concentration of sulfonic acid groups are those specified by the supplier (4.7 equiv./g), the TON was ranged from 4.6 to 4.9. The relatively constant TON for the catalyst weight less than equal to 4.5 wt.% suggested the absence of internal mass transfer limitations.

TABLE-3
EFFECT OF CATALYST WEIGHT OF 473 K PREHEATED
AMBERLYST 15 CATALYST THE TON ACHIEVED
AFTER 8 h OF REACTION IS ALSO MENTIONED

wt.% of catalyst (g)	Biodiesel yield (%)	TON
1.1	23	4.92
3.4	65	4.63
4.5	86	4.59

Reaction condition: T = 393 K; methanol:oil = 60:1; rpm = 750; Time = 8 h; reactant volume = 341 mL

Kinetic studies: The results showed that the physical structure of Amberlyst-15 catalyst preheated at 473 K was retained even when a methanol to oil ratio of 60:1 was used for biodiesel production. The effect of internal and external mass transfer is a concern for biodiesel production using heterogeneous catalysts. In present study, the use of tetrahydrofuran (THF) as a co-solvent did not have an effect on the biodiesel yield *versus* reaction time plot suggesting the absence of external mass transfer limitations. For the sake of simplicity, this plot is not shown. The presence of internal mass transfer limitations can also have an effect on the catalytic activity. The relatively constant TON with catalyst amount, as shown above, is indicative of the absence of internal mass transfer limitations. Furthermore, using established criteria for determining the effects of

internal and external mass transfer revealed the absence of severe transport limitations. Thus, the effect of transport limitations was neglected for the determination of kinetic parameters.

To determine the kinetic parameters for biodiesel production from Karanja oil, especially activation energy (E), it is necessary to study the effect of temperature. The effect of temperature was studied for the biodiesel production reaction with the 473 K preheated Amberlyst-15 catalyst and the results are shown in Fig. 6. As expected, the biodiesel yield increased with increase in time and temperature. After 8 h of reaction, the biodiesel yield achieved was 8% at 353K, 32% at 373K and 85% at 393 K. The rate of glyceride consumption (r_G) was calculated at different times and temperatures. From the value of r_G as function of reaction time, the values of rate constant (k) were obtained at different temperatures using integral analysis and the values of k and R^2 are tabulated in Table-4.
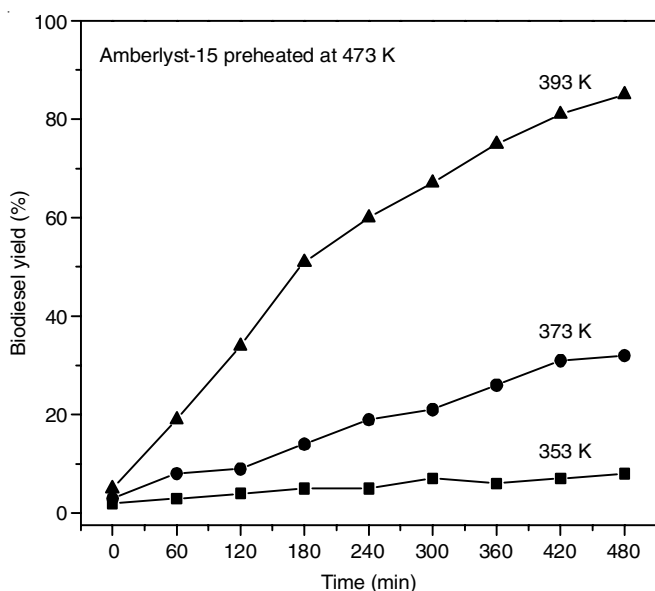

Fig. 6. Biodiesel yield as a function of time of reaction at different reaction temperatures. Reaction condition: methanol:oil = 60:1; rpm = 750; catalyst amount = 7.87 wt%; reactant volume = 341 mL

TABLE-4
RATE CONSTANTS FOR PREHEATED AMBERLYST 15 CATALYST OF THE DATA GIVEN IN Fig. 6 USING INTEGRAL ANALYSIS WITH n = 1

Reaction temp. (K)	k (h^{-1})	R^2
353	0.010 (6.491E-05)	0.999
373	0.044 (0.0025)	0.984
393	0.223 (0.0082)	0.993

While using integral analysis, the best fit was obtained for n = 1. The values of k at different temperatures were used to estimate the activation energy and a value of 89.36 kJ/mol was obtained. This value of activation energy was used as the initial guess for non-linear regression. Furthermore, the initial value of k_m and n required for non-linear regression were 0.0923 h^{-1} and 1, respectively. Using these initial values of the kinetic parameters, the values of k_m, E/R and n along with their 95% confidence limits were determined by non-linear regression and are presented in Table-5.

TABLE-5
PARAMETERS FOR THE RATE LAW FOR PREHEATED CATALYST USING NON-LINEAR REGRESSION

Variable	Initial guess	Value	95% confidence limit
k_m	0.0923	0.027	0.008
n	1	0.650	0.163
E/R	1.075E+04	1.043E+04	1710.9

The value of activation energy E was 86.98 kJ/mol, k_m was 0.027 h^{-1} and n was 0.65. Furthermore, the 95% confidence limits were much less than the parameter values. The parity plot between the experimental and model fitted data is shown in Fig. 7, which reveals a reasonable fit of the model with the experimental data.
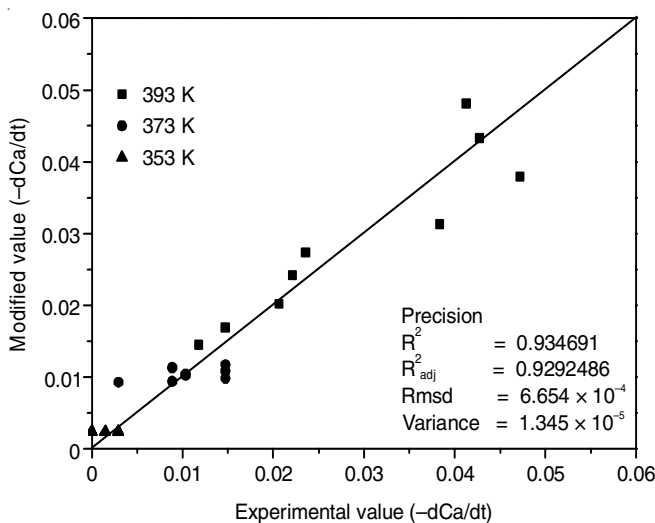

Fig. 7. Parity plot of preheated Amberlyst-15 for all the temperatures

For two esterification reactions using Amberlyst-15 catalyst, the activation energies of were 54.8 and 55.4 kJ/mol [19,29]. Furthermore, an overall activation energy of 60.7 kJ/mol for triacetin + oleic acid conversion using a heterogeneous catalyst and an activation energy of 120 kJ/mol for triolein conversion using Amberlyst-15 was also reported [30,31]. The activation energy the conversion of Karanja oil determined in the present study was in between the values reported previously. Furthermore, the activation energy of 86.98 kJ/mol was well in excess of those expected from the diffusion limited reactions. These observations suggest that mass transfer limitations were not present in the determination of kinetic parameters. Thus, the power law equation for the conversion of Karanja oil to biodiesel is

$$-r_G = 0.027 \exp\left[-(1.043E+4)\left(\frac{1}{T} - \frac{1}{373} \right) \right] C_G^{0.65} \quad (5)$$

Conclusion

Preheating the as-received Amberlyst-15 catalyst at 473 K for 4 h improved the biodiesel yield achieved from Karanja oil. By preheating the catalyst at 473 K the particle size decreased, the total and mesopore volume increased and no change in the sulfonic acid groups was observed. The sulphonic groups

were removed when heated at 573 K, thus 573 K preheated Amberlyst-15 catalyst showed little activity. The effect of catalyst amount revealed that beyond 4.5 wt.% catalyst did not increase the biodiesel yield. The preheated Amberlyst-15 catalyst at 473 K becomes deactivated with reuse, but could be regenerated by reheating at 473 K. The kinetic parameters for a power-law model revealed an order of reaction of 0.65, a reaction rate constant at 373 K of 0.0265 and activation energy of 86.98 kJ/mol. It appears that the kinetic parameters were devoid of the transport limitations.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. M.A.H. Shaah, M.S. Hossain, F.A.S. Allafi, A. Alsaedi, N. Ismail, M.O.A. Kadir and M.I. Ahmad, *RSC Adv.*, **11**, 25018 (2021); https://doi.org/10.1039/D1RA04311K

2. A.A. Kiss, A.C. Dimian and G. Rothenberg, *Adv. Synth. Catal.*, **348**, 75 (2006); https://doi.org/10.1002/adsc.200505160

3. P.K. Srivastava and M. Verma, *Fuel*, **87**, 1673 (2008); https://doi.org/10.1016/j.fuel.2007.08.018

4. K.V. Thiruvengadaravi, J. Nandagopal, V.S.S. Bala, S.D. Kirupha, P. Vijayalakshmi and S. Sivanesan, *Indian J. Sci. Technol.*, **2**, 20 (2009); https://doi.org/10.17485/ijst/2009/v2i12.4

5. Y.C. Sharma, B. Singh and J. Korstad, *J. Agric. Food Chem.*, **58**, 242 (2010); https://doi.org/10.1021/jf903227e

6. L.C. Meher, S.N. Naik and L.M. Das, *J. Sci. Ind. Res.*, **63**, 913 (2004).

7. M. Naik, L.C. Meher, S.N. Naik and L.M. Das, *Biomass Bioenergy*, **32**, 354 (2008); https://doi.org/10.1016/j.biombioe.2007.10.006

8. A.E. Atabani, A.S. Silitonga, H.C. Ong, T.M.I. Mahlia, H.H. Masjuki, I.A. Badruddin and H. Fayaz, *Renew. Sustain. Energy Rev.*, **18**, 211 (2013); https://doi.org/10.1016/j.rser.2012.10.013

9. F. Su and Y. Guo, *Green Chem.*, **16**, 2934 (2014); https://doi.org/10.1039/C3GC42333F

10. V.S.S. Bala, K.V. Thiruvengadaravi, P. Senthil Kumar, M.P. Premkumar, V. Vinoth kumar, S. Subash Sankar, M. Hari Kumar and S. Sivanesan, *Biomass Bioenergy*, **37**, 335 (2012); https://doi.org/10.1016/j.biombioe.2011.12.032

11. H.J. Berchmans and S. Hirata, *Bioresour. Technol.*, **99**, 1716 (2008); https://doi.org/10.1016/j.biortech.2007.03.051

12. S. Jain, M.P. Sharma and S. Rajvanshi, *Fuel Process. Technol.*, **92**, 32 (2011); https://doi.org/10.1016/j.fuproc.2010.08.017

13. J.A. Melero, J. Iglesias and G. Morales, *Green Chem.*, **11**, 1285 (2009); https://doi.org/10.1039/b902086a

14. A.P.S. Chouhan and A.K. Sarma, *Renew. Sustain. Energy Rev.*, **15**, 4378 (2011); https://doi.org/10.1016/j.rser.2011.07.112

15. M.O. Faruque, S.A. Razzak and M.M. Hossain, *Catalysts*, **10**, 1025 (2020); https://doi.org/10.3390/catal10091025

16. G. Arzamendi, I. Campo, E. Arguinarena, M. S'anchez, M. Montes and L.M. Gand'ýa, *Chem. Eng. J.*, **134**, 123 (2007); https://doi.org/10.1016/j.cej.2007.03.049

17. M.A. Harmer and Q. Sun, *Appl. Catal. A*, **221**, 45 (2001); https://doi.org/10.1016/S0926-860X(01)00794-3

18. W. Yu, K. Hidajat and A.K. Ray, *Appl. Catal., A*, **260**, 191 (2004); https://doi.org/10.1016/j.apcata.2003.10.017

19. M. Sharma, R.K. Wanchoo and A.P. Toor, *Ind. Eng. Chem. Res.*, **53**, 2167 (2014); https://doi.org/10.1021/ie402407r

20. E. Andrijanto, E.A. Dawson and D.R. Brown, *Appl. Catal. B*, **115-116**, 261 (2012); https://doi.org/10.1016/j.apcatb.2011.12.040

21. S.K. Karmee and A. Chadha, *Bioresour. Technol.*, **96**, 1425 (2005); https://doi.org/10.1016/j.biortech.2004.12.011

22. R. Kumar, P. Tiwari and S. Garg, *Fuel*, **104**, 553 (2013); https://doi.org/10.1016/j.fuel.2012.05.002

23. A.K. Gupta, *Chem. Biochem. Eng. Q.*, **32**, 1 (2018); https://doi.org/10.15255/CABEQ.2017.1201

24. G. Vicente, A. Coteron, M. Martinez and J. Aracil, *Ind. Crops Prod.*, **8**, 29 (1998); https://doi.org/10.1016/S0926-6690(97)10003-6

25. M.D. Guillen and A. Ruiz, *Trends Food Sci. Technol.*, **12**, 328 (2001); https://doi.org/10.1016/S0924-2244(01)00101-7

26. H.S. Fogler, Elements of Chemical Reaction Engineering, Prentice-Hall, Inc., Edn: 4, pp. 839-842 (2011).

27. K. Routray, K.R.S.K. Reddy and G. Deo, *Appl. Catal. A*, **265**, 103 (2004); https://doi.org/10.1016/j.apcata.2004.01.006

28. G. Fan, C. Liao, T. Fang, S. Luo and G. Song, *Carbohydr. Polym.*, **112**, 203 (2014); https://doi.org/10.1016/j.carbpol.2014.05.082

29. Y.-S. Huang and K. Sundmacher, *Int. J. Chem. Kinet.*, **39**, 245 (2007); https://doi.org/10.1002/kin.20236

30. D.E. López, J.G. Goodwin Jr., D.A. Bruce and S. Furuta, *Appl. Catal., A*, **339**, 76 (2008); https://doi.org/10.1016/j.apcata.2008.01.009

31. G. Paterson, T. Issariyakul, C. Baroi, A. Bassi and A. Dalai, *Catal. Today*, **212**, 157 (2013); https://doi.org/10.1016/j.cattod.2012.10.013